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Extremely narrow SiON angles in siloxy-substituted nitrogen-containing rings: a computational investigation†

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Quantum chemical calculations have been performed for a number of siloxy derivatives of pyrrolidine and piperidine in an attempt to gauge the effect of the saturated ring on the SiON angle. Most derivatives of pyrrolidine had SiON angles comparable to those previously observed for substituted *N,N*-dimethylhydroxylamines. However, piperidine derivatives were predicted to have particularly narrow SiON angles. *Anti, anti*, axial- F_3SiO -piperidine was found to have an angle of 82.9° , smaller than the narrowest angle observed by experiment in the gas phase, for $(\text{F}_3\text{C})\text{F}_2\text{SiONMe}_2$. The size of the ring and, in particular, the CNC angle appears to play a crucial role in determining the SiON angle. Further calculations including other heterocyclic rings were therefore performed to help explain this finding. Using the $(\text{F}_3\text{C})\text{F}_2\text{SiO}$ - group as a substituent on nitrogen allowed SiON angles of less than 80° to be calculated for several five-, six- and seven-membered rings.

Introduction

Although angles at oxygen atoms adjacent to silyl groups are usually wide, as in disiloxane, for which the SiOSi angle is 144.1° in the gas phase,¹ the angles in *O*-silyl hydroxylamines can be extremely narrow,^{2–7} as low as $84.4(32)^\circ$ in $(\text{F}_3\text{C})\text{F}_2\text{SiONMe}_2$.⁷ The study of these structures has produced many surprises, including very large effects of a single substituent on silicon (significant differences were observed between $\text{H}_3\text{SiONMe}_2$ ² and $\text{ClH}_2\text{SiONMe}_2$ ³), dramatic effects of changing the conformation of silyl-group substituents,³ and major contractions of SiON angles on crystallisation.³ In addition, computed angles are highly dependent on the level of theory used,⁴ and often do not reproduce the experimental results at all well.⁵

The research so far has concentrated mainly on the simplest representative compounds, and so the substituents on the nitrogen atom have usually been methyl groups, although CF_3 groups have also been used.³ We have therefore conducted a study, using computational methods, to investigate how the introduction of cyclic nitrogen-containing groups might influence the strengths of the $\text{Si} \cdots \text{N}$ interactions. Derivatives of pyrrole were included, to provide a reference point, as the involvement of the nitrogen electrons in the ring π system makes them unavailable for interaction with silicon. Pyrrolidine was then the comparable saturated five-membered ring parent compound, and piperidinyl groups were used to allow the effects of saturated ring size to be evaluated. In both the latter cases the ring conformation also had to be considered, as well as the position of the siloxy substituent—*endo/exo* or axial/equatorial as appropriate. To study the effect of the ring size further we then calculated structures with rings containing fewer than or more than five or six atoms.

We were not disappointed. There were more surprises, most particularly in the effect of the ring size on the SiON angles. Here we present the results of these calculations and some rationale for the forces driving narrower SiON angles.

Experimental

Quantum chemical calculations

Calculations were performed for many different siloxy derivatives of pyrrole, pyrrolidine and piperidine using the Gaussian 03 suite of programs.⁸ Geometry optimisations were carried out using Hartree–Fock (RHF), Møller–Plesset perturbation (MP2),⁹ and hybrid-DFT methods employing Becke's three-parameter exchange functional¹⁰ and the LYP¹¹ and PW91¹² correlation functionals. The Pople-type basis sets 3-21G,¹³ 6-31G¹⁴ and 6-311G¹⁵ were used with both diffuse (+) and polarisation (*) functions on both heavy and light atoms. Frequency calculations were performed using the RHF and hybrid-DFT methods to evaluate whether optimised structures represented minima (all real frequency values) on the potential-energy surface (PES). Angle scans (RHF/6-31G*) were performed on the SiON angles to obtain values for the energy barriers associated with widening or narrowing the angles.

Results

Pyrrole derivatives

Five siloxy derivatives of pyrrole were considered for theoretical investigation, namely H_3SiOR , FH_2SiOR , ClH_2SiOR , F_2HSiOR and F_3SiOR (R = pyrrolyl). The silyl functional groups were modelled so that the atom (usually a halogen; H in F_2HSiOR) that describes most easily the conformation of the silyl group was initially set to be *anti* to the donor nitrogen atom of the heterocyclic ring system ($\phi\text{XSiON} = 180^\circ$). All calculations suggested that the nitrogen atom was slightly pyramidal (sum of

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† Electronic supplementary information (ESI) available: Potential-energy scans for SiON angles, text, Tables S1–S2, Fig. S1; calculated coordinates, Tables S3–S30. See DOI: 10.1039/b805202f

angles approximately 358°), meaning that there are two possible ways that the planar ring can lie, with a dummy atom at the centre of the ring being *anti* or *syn* to O. We will only consider those molecules with the ring *anti* to O as no real *syn* structures were predicted.

From these initial geometries potential-energy scans were performed on $\phi\text{XSiO-N}$ ($\text{X} = \text{H}, \text{F}, \text{Cl}$) to verify that these conformers represented potential minima and also to search for other conformations of these molecules, where the atom on Si describing the conformation was *gauche* to N. For all pyrrole derivatives with mono- and dihalogenated silyl groups, both *anti* and *gauche* conformations were observed as minima (Fig. 1a).

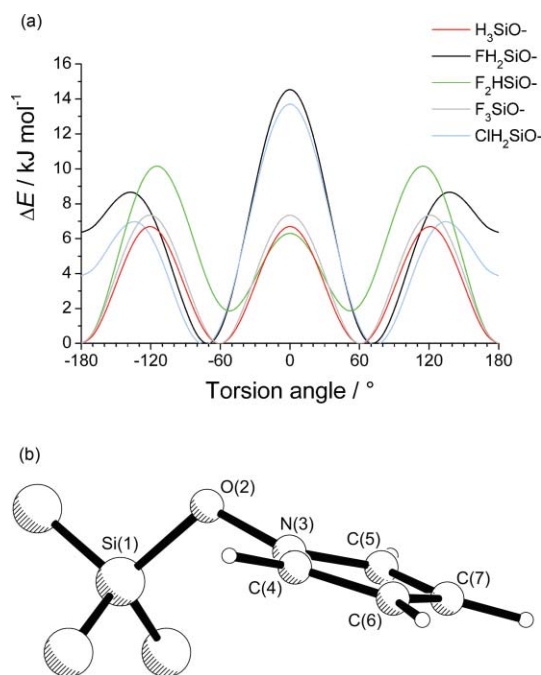


Fig. 1 (a) Potential-energy scans (RHF/6-31G*) for various siloxy derivatives of pyrrole, and (b) the structure of *anti, anti*-1- F_3SiO -pyrrole.

As one might expect, the potential-energy curves were very similar for the $\text{H}_3\text{SiO-}$ and $\text{F}_3\text{SiO-}$ and for the $\text{FH}_2\text{SiO-}$ and $\text{ClH}_2\text{SiO-}$ derivatives of pyrrole. For $\text{H}_3\text{SiO-pyrrole}$ and $\text{F}_3\text{SiO-pyrrole}$ the energy barriers between minima for the rotation of the silyl groups were very similar, although it is about 1 kJ mol^{-1} (RHF/6-31G*) higher in energy in the latter case. The energy differences between the *gauche* and *anti* conformers of $\text{FH}_2\text{SiO-pyrrole}$ and $\text{ClH}_2\text{SiO-pyrrole}$ are 7 and 4 kJ mol^{-1} (RHF/6-31G*), respectively. Therefore, from the initial scans, it was concluded that the *gauche* conformers were more stable. The potential-energy curve for $\text{F}_2\text{HSiO-pyrrole}$ looks different to the other four, as it does not have a global minimum at around 60° . This is simply because the unique atom is H; the more stable form (by 2 kJ mol^{-1}) has an *anti* halogen atom, like all the other derivatives studied.

Pyrrolidine derivatives

Due to the nature of the saturated (and therefore non-planar) ring system of pyrrolidiny, both *endo* and *exo* conformers are possible (Fig. 2b and c). The number of conformers that could be feasible

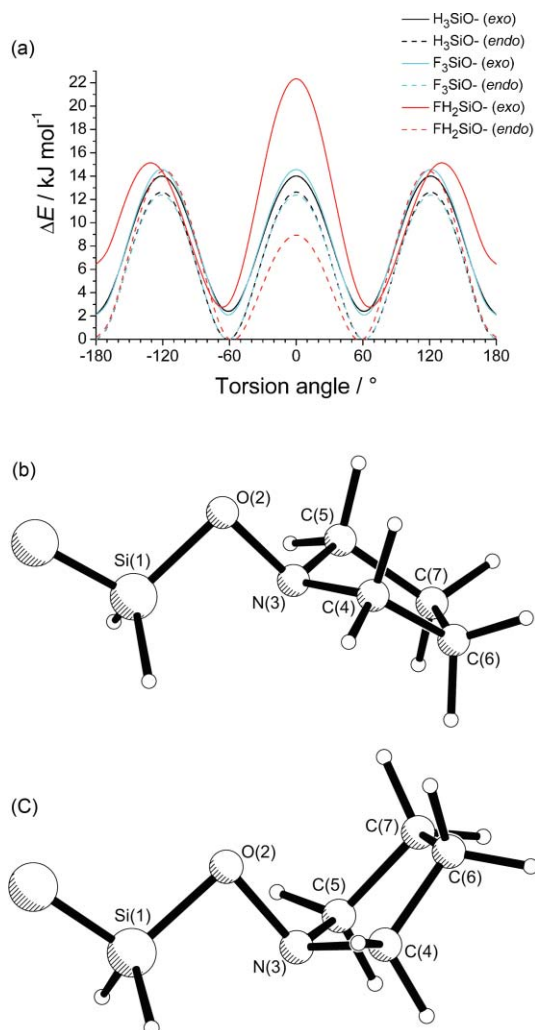


Fig. 2 (a) Potential-energy scans (RHF/6-31G*) for various siloxy derivatives of pyrrolidine with the oxygen atom *endo* or *exo* to the ring, (b) the structure of *anti, anti, exo*-1- FH_2SiO -pyrrolidine, and (c) the structure of *anti, anti, endo*-1- FH_2SiO -pyrrolidine. *Exo* and *endo* conformers are shown on a common energy scale.

for any one derivative is therefore twice that for the equivalent pyrrole derivative, even with the assumption that the ring has an envelope conformation, with the nitrogen atom positioned at the apex of the flap. For this reason only three siloxy derivatives were chosen for theoretical investigation. These were H_3SiOR , FH_2SiOR , and F_3SiOR ($\text{R} = \text{pyrrolidiny}$), each with the oxygen atom *endo* and *exo* to the ring.

If different conformations have to be taken into account for the silyl moiety then, for example, a *gauche, anti, endo* conformation would describe first the position of the silyl substituent determining the conformation, *i.e.* the substituent determining the conformation of the silyl group is *gauche* to N(3), secondly the position of Si relative to the bisector of the C(4)NC(5) angle, which is *anti* for the molecules presented here, and thirdly the position of the oxygen atom relative to the ring, which can be either *endo* or *exo*.

Again the silyl groups were modelled in the highest symmetry possible and one of the substituents was set *anti* to the donor nitrogen atom of the heterocyclic ring system. Potential-energy

Table 1 Energy differences (ΔE , MP2/6-311++G**) between the *endo* and *exo* conformers of some pyrrolidine derivatives, and between axial and equatorial conformations of piperidine derivatives^a

Molecule	ΔE^b
<i>anti</i> , <i>anti</i> -1-H ₃ SiO-pyrrolidine	2.1
<i>anti</i> , <i>anti</i> -1-F ₃ SiO-pyrrolidine	2.1
<i>anti</i> , <i>anti</i> -1-FH ₂ SiO-pyrrolidine	2.9
<i>gauche</i> , <i>anti</i> -1-FH ₂ SiO-pyrrolidine	1.5
<i>anti</i> , <i>anti</i> -1-H ₃ SiO-piperidine	6.6
<i>anti</i> , <i>anti</i> -1-F ₃ SiO-piperidine	5.7

^a Energies in kJ mol⁻¹. ^b $\Delta E = E_{\text{endo/axial}} - E_{\text{exo/equatorial}}$.

scans about ϕXSiON (X = H, F) were performed to verify that these *anti*, *anti* structures represented minima for both *endo* and *exo* conformers and also to search for other stable conformations (Fig. 2a).

In this discussion we will first consider structures with the oxygen atom *endo* to the ring. The potential-energy scans for *anti*, *anti*-H₃SiO-pyrrolidine and *anti*, *anti*-F₃SiO-pyrrolidine showed that each has only one conformer, with one H/F *anti* to the nitrogen atom. Interestingly, the potential-energy calculations predict almost identical energy barriers for rotation of SiX₃ for *anti*, *anti*-H₃SiO-pyrrolidine and *anti*, *anti*-F₃SiO-pyrrolidine. The scan for the FH₂SiO derivative predicts the *gauche*, *anti* conformer to be the lower-energy conformer. The potential-energy scans for the equivalent *anti*, *anti*-H₃SiO and *anti*, *anti*-F₃SiO derivatives with the oxygen atoms in the *exo* position relative to the ring system exhibit the same features as described above. However, because of the position of the ring system relative to oxygen, the barrier between the two *gauche*, *anti* forms of the *exo*-FH₂SiO derivative was reduced and the barrier for conversion to the *anti*, *anti* form increased. In addition, the *anti*, *anti* and *gauche*, *anti* forms of *exo*-FH₂SiO-pyrrolidine had the same energy. Subsequent geometry optimisations and frequency calculations showed that these structures represented minima on the potential-energy curves, *i.e.* all frequencies were real. All *anti*, *anti* conformers had XSiON (X = H, F, Cl) torsion angles of 180°. All *anti*, *anti* conformers, including the H₃SiO- and F₃SiO-derivatives, had C_s symmetry and the *gauche*, *anti* conformers had C₁ symmetry. At the MP2/6-311++G** level the *endo* conformers were lower in energy by approximately 2 kJ mol⁻¹ for each of the molecules studied (Table 1). Potential-energy scans of the SiON angles for the respective conformations of both derivatives were performed to gain more information about the flexibility of these angles. The results of these scans are included in the electronic Supplementary Information, ESI,[†] where they are also discussed.

Piperidine derivatives

Because of the large number of possible conformations adopted by siloxy derivatives of piperidine, a preliminary investigation was performed for piperidine itself. Piperidine can adopt six different conformations, *i.e.* one chair and two boat configurations of the ring, each with the NH bond axial or equatorial. First, boat configurations with the nitrogen positioned on the “stern” and on the “hull” were considered, but calculations at the RHF/6-311++G** level did not yield any potential-energy minimum. The two chair configurations of piperidine did represent minima,

having only real frequencies. The energy differences between the boat conformers and the lowest-energy conformation (that of the chair with hydrogen in the equatorial position) were in excess of 30 kJ mol⁻¹. Based on these findings, it was decided to focus the investigation of the siloxy-piperidine derivatives on the chair conformations only.

Two derivatives, *anti*, *anti*-H₃SiO-piperidine and *anti*, *anti*-F₃SiO-piperidine, were studied to estimate the strength of the N...Si interactions in silyl compounds with piperidinyl as donor group. The molecules were modelled with C_s symmetry for the silyl group, with one substituent *anti* to the donor nitrogen atom of the piperidinyl ring. Potential-energy scans were performed to deduce whether the *anti* position of one substituent on silicon in relation to the piperidinyl nitrogen was correct (Fig. 3a). For structures with both equatorial and axial oxygen atoms only one conformation is predicted in each case (with $\phi\text{H/FSiON} = 180^\circ$). The conformations with the oxygen atom in an axial position relative to the ring system exhibited marginally higher

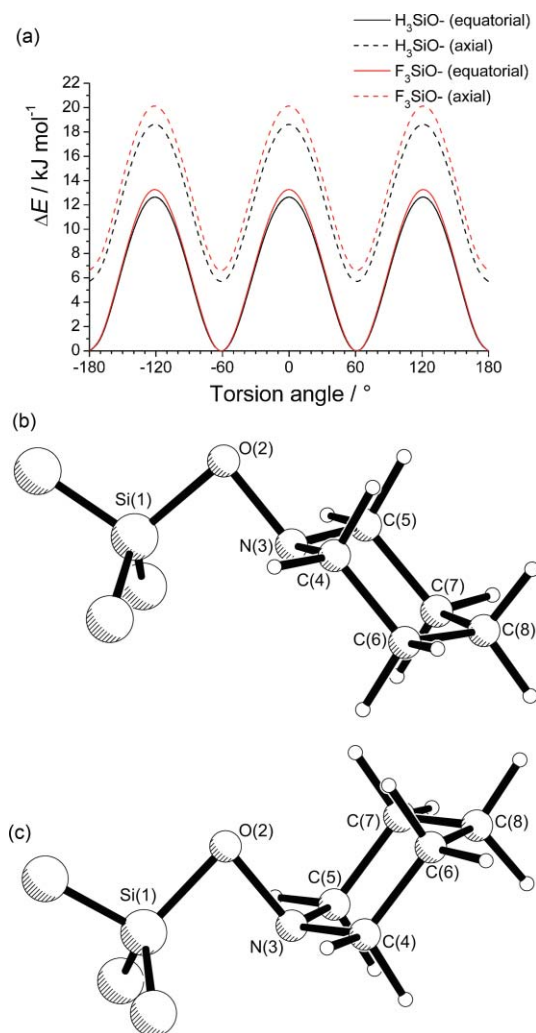


Fig. 3 (a) Potential-energy scans (RHF/6-31G*) for various siloxy derivatives of piperidine in its chair form, with the oxygen atom axial or equatorial to the ring, (b) the structure of *anti*, *anti*-1-F₃SiO-piperidine, and (c) the structure of *anti*, *anti*-axial-1-F₃SiO-piperidine. Axial and equatorial conformers are shown on a common energy scale.

potential-energy barriers than their equatorial counterparts. In all cases the energy barrier was calculated to be in excess of 12.5 kJ mol⁻¹. Subsequent geometry optimisations and frequency calculations verified that these structures existed as potential minima and both derivatives had C_s symmetry. At the MP2/6-311++G** level the equatorial conformer of *anti, anti*-1-F₃SiO-piperidine was lower in energy by 5.7 kJ mol⁻¹ and that of *anti, anti*-1-H₃SiO-piperidine was lower in energy by 6.6 kJ mol⁻¹ (Table 1). Potential-energy scans of the SiON angles for the respective conformations of both derivatives were performed to gain more information about the flexibility of these angles. This is discussed in detail in the ESI.†

As the presence of a nitrogen atom in a piperidine ring seems to facilitate extremely narrow SiON angles, it seemed possible that an SiON angle narrower than that in (F₃C)F₂SiONMe₂ [84.4(32) from GED⁷] could be achieved for (F₃C)F₂SiO-piperidine. At the MP2/6-311++G** level it was found that the SiON angle in (F₃C)F₂SiO-piperidine was 78.4°.

Other ring systems

In an attempt to account for the apparent trend of narrowing SiON angle with increasing size of ring we extended our study to include three- and four-membered rings (aziridinyl and azetidiny), six-membered rings with nitrogen and one more heteroatom present (piperazinyl, morpholinyl and thiomorpholinyl) and a seven-membered ring (1-aza-cyclohepta-4-en-1-yl). For each of these rings we calculated (MP2/6-311++G**) the structure with the (F₃C)F₂SiO- group on the nitrogen for the lowest energy conformer. Each of these molecules is depicted in Fig. 4.

For the six-membered rings we studied only the *anti, anti*, equatorial conformers, which were lower in energy than their *anti, anti*, axial counterparts. For the 1-aza-cyclohepta-4-en-1-yl derivative we studied only *anti, anti, exo* conformers, although because of the seventh atom in the ring, additional conformers are possible. As well as a C_s-symmetric molecule, in which the planar CH₂CH=CHCH₂ part of the ring lies so as to form a chair configuration (see Fig. 4), a half-twist of this configuration gives a conformer with C₂ local ring symmetry. There is also a boat configuration, but it is more than 1000 kJ mol⁻¹ higher in energy than the other two. Here we will concentrate on the chair conformer, as it is 5.5 kJ mol⁻¹ lower in energy (MP2/6-311++G**) than the half-twist conformer.

Discussion

As far as we are aware, until now no cyclic systems of these kinds have been investigated, probably because they were not readily available or were expected to show effects similar to those observed in siloxy-*N,N*-dimethylamines. However, the investigation of N-containing ring systems to see how this affected the strengths of the Si...N interactions in siloxy derivatives of those rings has yielded some interesting results.

The series of siloxy derivatives of pyrrole was studied as a reference point from which the effects of the saturated nitrogen-containing rings could be measured. As expected, they showed no acute angle contractions like those seen for siloxy amines and silylhydrazines. Even when the silyl group was monofluorinated the SiON angle was fairly wide (109.6°; Table 2).

Table 2 Calculated SiON angles (MP2/6-311++G**) for various silyl compounds. Values shown in this table are those for conformers with the smallest SiON angles

Molecule	∠SiON/°
<i>anti, anti</i> -H ₃ SiO-NMe ₂	102.5
<i>anti, anti</i> -FH ₂ SiO-NMe ₂	90.0
<i>anti, anti</i> -F ₃ SiO-NMe ₂	94.1
<i>anti, anti</i> -H ₃ SiO-pyrrole	112.8
<i>anti, anti</i> -FH ₂ SiO-pyrrole	109.6
<i>anti, anti</i> -F ₃ SiO-pyrrole	113.2
<i>anti, anti, endo</i> -H ₃ SiO-pyrrolidine	102.7
<i>anti, anti, endo</i> -FH ₂ SiO-pyrrolidine	90.7
<i>anti, anti, endo</i> -F ₃ SiO-pyrrolidine	93.8
<i>anti, anti, axial</i> -H ₃ SiO-piperidine	101.3
<i>anti, anti, axial</i> -F ₃ SiO-piperidine	82.9

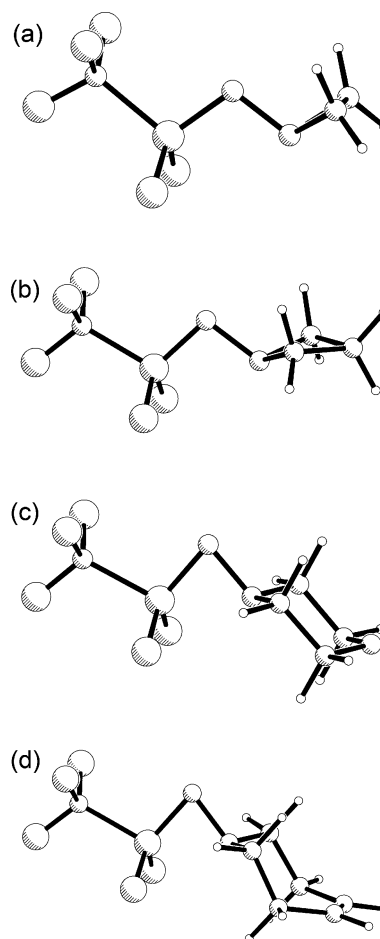


Fig. 4 Molecular structures of (a) (F₃C)F₂SiO-aziridine, (b) (F₃C)F₂SiO-azetidine, (c) (F₃C)F₂SiO-morpholine, demonstrating the conformation adopted by all six-membered rings, and (d) (F₃C)F₂SiO-1-aza-cyclohepta-4-en-1-yl.

For comparison we also performed calculations for molecules in which the nitrogen atom was part of an NMe₂ group. In terms of its influence on the SiON angle, the pyrrolidine group appears to have properties very similar to the *N,N*-dimethylamino group, including the same trend of angle contractions with varying silyl substituents. Interestingly, the position of the oxygen atom (*endo* or *exo* with respect to the pyrrolidine ring) did not have a substantial effect on the ability of pyrrolidine to promote angle contraction.

Table 3 Calculated CNC and SiON angles (MP2/6-311++G**) for various (F₃C)F₂SiO- compounds. Values shown in this table are those for conformers with the smallest SiON angles^a

Molecule	∠CNC/°	∠SiON/°
<i>anti, anti</i> -(F ₃ C)F ₂ SiO-aziridine	60.7	106.9
<i>anti, anti, exo</i> -(F ₃ C)F ₂ SiO-azetidine	90.2	95.9
<i>anti, anti, axial</i> -(F ₃ C)F ₂ SiO-pyrrolidine	105.5	79.4
<i>anti, anti, exo</i> -(F ₃ C)F ₂ SiO-morpholine	110.8	80.8
<i>anti, anti, exo</i> -(F ₃ C)F ₂ SiO-piperazine	111.8	79.0
<i>anti, anti, exo</i> -(F ₃ C)F ₂ SiO-piperidine	112.4	78.4
<i>anti, anti, exo</i> -(F ₃ C)F ₂ SiO-thiomorpholine	113.5	79.7
<i>anti, anti, exo, chair</i> -(F ₃ C)F ₂ SiO-1-azacyclohept-4-en-1-yl	115.7	78.1

^a Coordinates for each of these structures are given in Tables S23–S30.†

In contrast to the calculations for the pyrrolidine derivatives, the calculations on the trifluorosilyl derivatives of piperidine showed a more marked dependence on the position of O relative to the ring. *Anti, anti*, equatorial-F₃SiO-piperidine has an SiON angle that is 3° wider than that in the corresponding *anti, anti*, axial conformer. The siloxy derivative displayed an SiON angle similar to that of siloxy-*N,N*-dimethylamine. Interestingly, *anti, anti*, axial-F₃SiO-piperidine was predicted to have an SiON angle narrower than that reported for any trifluorosilyl compound in the literature. In fact, the calculated SiON angle (MP2/6-311++G**) for *anti, anti*, axial-F₃SiO-piperidine is, at 82.9°, slightly narrower than that of (F₃C)F₂SiONMe₂,⁷ which currently has the narrowest experimentally determined SiON angle in the gas phase [84.4(32)°]. Given data presented here it seemed possible that an SiON angle narrower than that in (F₃C)F₂SiONMe₂ could be achieved for (F₃C)F₂SiO-piperidine. Indeed, when this was calculated at the MP2/6-311++G** level the SiON angle was found to be 78.4°.

As the size of the ring seems to be important to the SiON angle, further calculations were performed (also at the MP2/6-311++G** level) with the (F₃C)F₂SiO- group attached to the nitrogen atoms in other rings. In general it should be expected that, as the rings containing fewer atoms have narrower CNC angles than in the six-membered ring, they could have wider SiON angles. Similarly, we might expect that seven-membered rings, where CNC should be slightly wider than in six-membered rings, will promote narrower SiON angles.

The size of the ring appears to be crucial to the size of the SiON angle. Table 3 gives both the internal CNC ring angle and the SiON angle for every structure with the (F₃C)F₂SiO- group, and the correlation between the two angles is shown in Fig. 5. A simple explanation for this correlation is that a wider angle in the ring will be associated with lower nitrogen p orbital character in the two N–C bonds, and therefore with more p character in the nitrogen ‘lone pair’, increasing the interaction with silicon.

Conclusion

The theoretical investigation of both pyrrolidinyl and piperidinyl derivatives has identified some remarkable capabilities for angle contraction. It now seems appropriate to broaden the spectrum of silyl compounds and try to synthesise molecules with pyrrolidinyl and piperidinyl as donor groups and to determine their experimental structures both in the gas phase and as crystals.

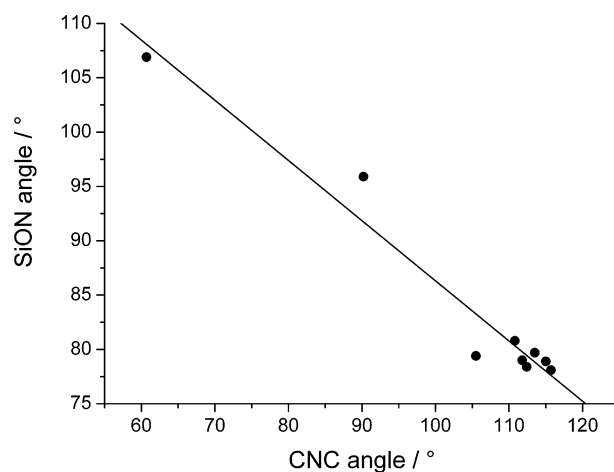


Fig. 5 Graphical representation of the dependence of SiON angle on CNC angle for all compounds listed in Table 3.

From the data it is expected that silyl compounds with NMe₂ and pyrrolidinyl donor groups should have fairly similar chemical properties because both show very narrow SiON angles. Similar considerations apply to silyl compounds with piperidinyl as a donor group, although as the SiON angles will probably be more acute substituted piperidines might be more reactive than molecules with NMe₂ and pyrrolidine groups.

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